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CATALYTIC TREATMENT OF GASEOUS EFFLUENTS
CONTAINING VARYING AMOUNTS OF SULFUR COMPOUNDS

BACKGROUND OF THE INVENTION

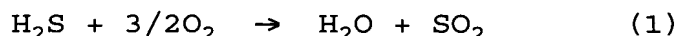
Technical Field of the Invention:

5 The present invention relates to novel
catalysts for the purification/treatment of gases,
especially of gaseous industrial effluents containing
sulfur compounds, particularly to recover elemental
sulfur therefrom, and, more especially, to novel
10 catalysts for the Claus reaction and/or the hydrolysis
of organic sulfur compounds.

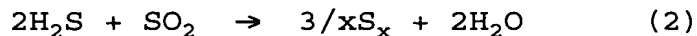
Description of the Prior Art:

 In the conventional Claus process, the
recovery of sulfur from gases containing hydrogen
15 sulfide and, optionally, organic sulfur compounds
comprises two stages.

 In a first step, the hydrogen sulfide is
burned in the presence of a controlled amount of air to
convert a proportion of the hydrogen sulfide into sulfur
20 dioxide according to the following reaction mechanism
(1):

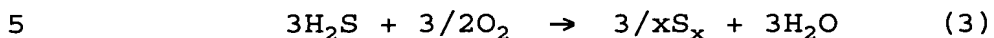


 and then, in a second step, the gaseous mixture obtained
is passed through converters, in series, containing a
25 catalyst bed wherein the actual Claus reaction (2):



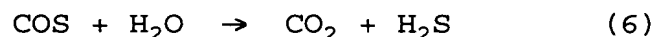
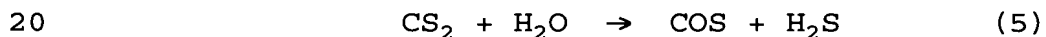
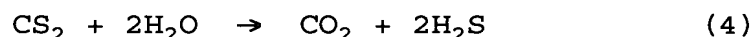
is carried out.

The overall balance of the reaction is therefore (3):



Furthermore, other than hydrogen sulfide, the gases may contain organic sulfur compounds such as CS_2 and COS , which are generally stable in the catalytic converters and which contribute to an increase of 20% to 50% in the emissions of SO_2 and of sulfur compounds into the atmosphere after the fumes have been incinerated. These very objectionable compounds are either already present in the gas to be treated, or are formed during the first oxidation step which is conducted at elevated temperature.

These compounds can be removed via several types of reactions, in particular by hydrolysis according to the mechanisms:



this being to limit the discharge of toxic effluents at the downstream end of a sulfur plant.

These reactions are also effected in a catalyst bed, advantageously using a catalyst based on titanium, cerium oxide or zirconium oxide, or alumina.

They are generally carried out simultaneously with the Claus reaction (2) in such converters.

For this purpose, the catalysts employed must exhibit the best possible activities, as well as the best resistance to the stresses experienced during use, as a function of time.

5 Alumina is commonly employed as a catalyst for these applications. One of the principal reasons for its deactivation is due to the concomitant formation of sulfates at its face surfaces, which sulfates reduce its catalytic performance, frequently drastically.

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SUMMARY OF THE INVENTION

It has now unexpectedly been determined that the extent of the sodium content of alumina is a primary factor in the deactivation thereof, especially by sulfate formation.

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Accordingly, a major object of the present invention is the provision of novel alumina catalysts comprising an amount of sodium values which is within a certain judiciously selected range.

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Briefly, the present invention thus features a catalyst for the treatment/purification of gases containing objectionable amounts of sulfur compounds and/or for the hydrolysis of organic sulfur compounds, essentially consisting of a catalytically active alumina which comprises sodium values, the sodium content of the alumina ranging from 1,200 ppm to 2,700 ppm of Na_2O by weight thereof.

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BRIEF DESCRIPTION OF THE DRAWING

The Figure of Drawing is a graph plotting the conversion of CS_2 as a function of the Na_2O content in various alumina catalysts.

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**DETAILED DESCRIPTION OF BEST MODE AND
PREFERRED EMBODIMENTS OF THE INVENTION**

More particularly according to the present invention, the particular Na_2O concentration range was completely unexpected and surprising insofar as the state of this art mandated sodium contents that were as low as possible because of the detrimental effect of Na_2O vis-a-vis alumina over the course of a Claus reaction.

The sodium content of the alumina of the catalysts according to the invention advantageously ranges from 1,500 ppm to 2,500 ppm and preferably from 1,700 to 2,200 ppm.

The catalysts of this invention include alumina containing sodium as the catalytically active component, in a weight proportion which advantageously ranges from 0.5% to 100% (of alumina + sodium), and preferably from about 60% to 99%, relative to the total weight of the final catalyst.

The catalysts according to the present invention may also include, in a proportion which is smaller in relation to the alumina, other oxides such as titanium dioxide, silica, zirconium oxide, cerium oxide, tin oxide, oxides of trivalent rare earths, molybdenum oxide, cobalt oxide, nickel oxide, iron oxide, and the like.

The oxides other than alumina may constitute from 0% to 40% of the weight of the catalyst.

The catalysts of the invention may additionally include one or more constituents selected from among the clays, silicates, alkaline earth metal or ammonium sulfates, ceramic fibers, asbestos fibers, etc.

They may also include additives for facilitating the forming or shaping thereof and additives for improving their final mechanical properties.

Particularly exemplary such additives include cellulose, carboxymethyl cellulose, carboxyethyl cellulose, tallol, xanthan gums, surface-active agents, flocculating agents such as polyacrylamides, carbon black, starches, stearic acid, polyacrylic alcohol, polyvinyl alcohol, biopolymers, glucose, polyethylene glycols, and the like.

The alumina employed for the catalyst according to the invention may be prepared, as described in FR-A-2,527,197, via treatment, in an aqueous medium which has a pH lower than 9, of an active alumina powder obtained by rapid dehydration of hydrargillite in a stream of hot gases, spray-drying and then calcining according to the technique described in EP-A-15,196.

It is also advantageously prepared, as described in FR-A-2,449,650, via treatment of an active alumina powder which has a poorly crystallized and/or amorphous structure in an aqueous medium which has a pH lower than 9, an alumina of "poorly crystallized structure" being as defined therein.

The alumina according to the invention may also be prepared by mixing an alumina obtained according to the process described in FR-A-2,449,650 with an alumina obtained according to the process described in FR-A-2,527,197, comprising a rapid dehydration of

aluminum hydroxides or oxyhydroxides and, more particularly, of hydrargillite in a stream of hot gases. This rapid dehydration is carried out in any suitable apparatus, by means of a stream of hot gases, the inlet
5 temperature of the gases into the apparatus generally ranging from approximately 400° to 1,200°C, and the time of contact of the hydroxide or oxyhydroxide with the hot gases generally ranging from a fraction of a second to 4-5 seconds. This process is described in greater
10 detail in FR-A-1,108,011. The mixture of an alumina obtained by the process described in FR-A-2,449,650 with an alumina obtained by the process described in FR-A-2,527,197 permits, merely by adjusting the proportion of each of the aluminas thus obtained, the
15 preparation of a final alumina exhibiting the desired Na₂O content. Indeed, an alumina prepared by rapid calcining of aluminum hydroxides or oxyhydroxides produces an alumina which has a high Na₂O content, on the order of 3,500 ppm. After treatment in an aqueous
20 medium at a pH lower than 9, the Na₂O content is considerably decreased (less than 1,000 ppm). The addition of alumina prepared according to the second of the above processes then enables production of an alumina which has an Na₂O content of from 1,200 ppm to
25 2,700 ppm.

The catalyst according to the invention is next converted into any appropriate form or shape, optionally after impregnation onto a typically refractory support.

30 For example, the catalyst may be shaped by kneading the various constituents of the catalyst and extruding the inorganic paste thus obtained, by tabletting, by shaping into the form of beads using a rotary coating pan or a drum, or by any other known
35 means for agglomerating a powder containing alumina and,

optionally, other ingredients selected from among those indicated above.

It may also comprise an alumina to which other ingredients have optionally been added and which is
5 merely crushed; thus, it does not have any special form.

It is advantageous, however, that the alumina be in the form of beads having a diameter ranging from 1.5 to 10 mm and preferably from 3 to 7 mm.

The catalysts according to the present
10 invention are highly efficient, both for catalyzing the Claus reaction (equation (2)), as well as reactions of hydrolysis of organic sulfur compounds (equations (4), (5) and (6)).

Thus, the present invention therefore also
15 features the use of a catalyst as described above for treating gases containing objectionable or contaminating amounts of sulfur compounds for the production of elemental sulfur, via Claus reaction, and for treating gases containing organic sulfur compounds via a
20 hydrolysis reaction.

This invention lastly features processes for the treatment of gases containing sulfur compounds via Claus reaction or via hydrolysis, by passing these gases over a catalyst bed, at least a proportion of the
25 catalyst comprising a catalyst as described above.

In order to further illustrate the present invention and the advantages thereof, the following specific examples are given, it being understood that same are intended only as illustrative and in nowise
30 limitative.

In said examples to follow, the activity or efficacy of the catalysts was as shown on the attached Figure of Drawing, plotting the conversion of CS_2 as a function of the Na_2O content in the catalysts according
35 to the invention.

EXAMPLE 1:

Hydrargillite was dehydrated rapidly at 1,000°C by means of a stream of hot gas to obtain a product A. A contained 3,600 ppm of Na₂O. A proportion
5 of product A was treated in an aqueous medium according to the process described in EP-A-15,196, to provide a product B; its Na₂O content was then 800 ppm by weight. A 50:50 mixture of aluminas A and B was formulated, then granulated into beads having a diameter of from 3.1 to
10 6.3 mm. These beads then had a sodium content of 2,200 ppm by weight, expressed as Na₂O.

EXAMPLE 2:

Catalysts which had Na₂O contents equal to 400, 600, 1,200, 1,700, 2,200, 2,700, 3,000 and 3,700
15 ppm were prepared according to the procedure of Example 1.

All of the catalysts exhibited the following physicochemical characteristics: specific surface: 360 (± 10)m²/g, bead particle size: 3.1 - 6.3 mm, pore
20 volume of pores of diameter greater than 0.1 μm: 18.5 ml/100 g of alumina, pore volume of pores of diameter greater than 1 μm: 15.5 ml/100 g of alumina.

These catalysts were tested for their activity in the first reactor (R₁) and in the second reactor (R₂)
25 in a Claus process. Thus, the Claus unit comprised two identical reactors R₁ and R₂, which were placed in series and charged with the same catalyst, the gas to be treated being introduced successively into R₁ and then R₂.

In R_1 the reaction which was crucial, being the most difficult to complete, was the hydrolysis of COS and, primarily, of CS_2 . In R_2 the lower temperature and the lower H_2S content rendered the traditional Claus reaction more discriminating, because of the more preoccupying problems related to the formation of alumina sulfate.

The trends determined in hydrolysis of CS_2 in R_1 and in the Claus reaction in R_2 were apparent: if a catalyst A was more efficient than a catalyst B in R_1 , then A was also more efficient than B in R_2 .

Accordingly, only the results of catalysis of the hydrolysis of CS_2 in reactor R_1 are reported here.

The tests for catalytic activity were conducted by contacting with the catalysts a gas whose composition by volume was the following:

H_2S	6%
SO_2	4%
CS_2	1%
H_2O	30%
N_2	59%

The contacting was in a reactor at $320^\circ C$, operating isothermally, with an oxygen content of 10 ppm by volume and utilizing a contact time of 2 s (under standard temperature and pressure conditions (STPC)).

For an identical reactor volume filled with catalyst and an identical inlet flow rate of gas to be treated, the performance of the different catalysts was compared by measuring the hydrolysis activity and by analyzing, using gas phase chromatography, the H_2S , the SO_2 , the COS and the CS_2 present in the gases exiting the reactor.

The CS₂ conversion was thus measured after a steady state had been obtained in the content of reaction products exiting the reactor.

5 In each catalyst test, the CS₂ conversion corresponding to the catalyst employed was measured.

The results are illustrated in the attached Figure of Drawing, which shows that, with the Na₂O range of from 1,200 to 2,700 ppm, the conversion of CS₂ was highly advantageous.

10 This conversion was more particularly advantageous over the range which is preferred according to this invention, of from 1,700 to 2,200 ppm.

While the invention has been described in terms of various preferred embodiments, the skilled
15 artisan will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims,
20 including equivalents thereof.